

AUSTRALIA

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the persons identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] Applicant: ELF ATOCHEM SA
 Address: 4 & 8 COURS MICHELET, LA DEFENSE 10, 92800 PUTEAUX, FRANCE

[70] Nominated Person: ELF ATOCHEM SA
 Address: 4 & 8 COURS MICHELET, LA DEFENSE 10, 92800 PUTEAUX, FRANCE

[54] Invention Title: STABLE AQUEOUS DISPERSION OF HYDROXYLATED FLUORINATED COPOLYMERS AND OF ACRYLIC COPOLYMERS, PROCESS FOR ITS PREPARATION AND ITS USE AS AN AQUEOUS-PHASE PAINT

[72] Name(s) of actual inventor(s): PATRICK KAPPLER, JEAN-LUC PERILLON and CATHERINE SAVARY

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of
 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: WM

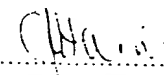
BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
94 06682	FR	FR	1 JUNE 1994

Basic Applicant(s): ELF ATOCHEM SA

Drawing number recommended to accompany the abstract

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS


 Carolyn J. Harris
Registered Patent Attorney

DATED this 30th day of May 1995.

4068904 300595



AU9520376

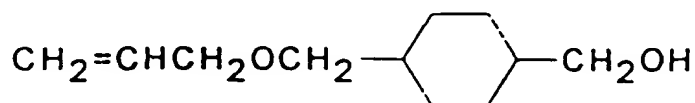
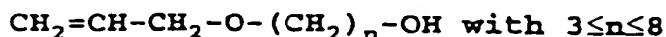
(12) PATENT ABSTRACT (11) Document No. AU-A-20376/95
(19) AUSTRALIAN PATENT OFFICE

- (54) Title
STABLE AQUEOUS DISPERSION OF HYDROXYLATED FLUORINATED COPOLYMERS AND OF ACRYLIC COPOLYMERS, PROCESS FOR ITS PREPARATION AND ITS USE AS AN AQUEOUS-PHASE PAINT
- (51)⁵ International Patent Classification(s)
C08L 027/16 C08J 003/03 C08L 027/12 C08L 027/18
- (21) Application No. : 20376/95 (22) Application Date : 30.05.95
- (30) Priority Data
- (31) Number (32) Date (33) Country
94 06682 01.06.94 FR FRANCE
- (43) Publication Date : 07.12.95
- (71) Applicant(s)
ELF ATOCHEM SA
- (72) Inventor(s)
PATRICK KAPPLER; JEAN-LUC PERILLON; CATHERINE SAVARY
- (74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS, Locked Bag 5, HAWTHORN VIC 3122
- (57) Claim

1. Stable aqueous dispersion comprising at least one emulsifying agent, characterized in that it comprises one or a number of hydroxylated fluorinated copolymers derived from the following monomers.

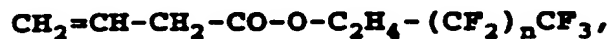
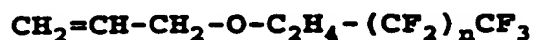
1. from 45 to 95 % (molar) of vinylidene fluoride (VF2) and/or of trifluoroethylene (VF3),
2. from 5 to 55 % (molar) of tetrafluoroethylene (C₂F₄)

3. from 2 to 25 mol, per 100 mol of monomers 1 + 2, of one or a number of hydroxylated allylic monomers chosen from allylic alcohol and hydroxylated allylic ethers such as





4. and from 0 to 10 mol, per 100 mol of monomers 1 + 2, of one or a number of monomers chosen from non-hydroxylated vinyl ethers, such as butyl vinyl ether, other fluorinated monomers (i.e. other than VF2, VF3 or C_2F_4), such as C_3F_6 or $\text{C}_2\text{F}_3\text{Cl}$, or non-salified allylic ethers and esters which are optionally carboxylated and/or substituted with $-(\text{CF}_2)_n-\text{CF}_3$ with $4 \leq n \leq 10$, such as:



AUSTRALIA

Patents Act 1990

**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Application Number:

Lodged:

Invention Title:

STABLE AQUEOUS DISPERSION OF HYDROXYLATED FLUORINATED
COPOLYMERS AND OF ACRYLIC COPOLYMERS, PROCESS FOR ITS
PREPARATION AND ITS USE AS AN AQUEOUS-PHASE PAINT

The following statement is a full description of this invention, including the
best method of performing it known to us :-

STABLE AQUEOUS DISPERSION OF HYDROXYLATED FLUORINATED
COPOLYMERS AND OF ACRYLIC COPOLYMERS, PROCESS FOR ITS
PREPARATION AND ITS USE AS AN AQUEOUS-PHASE PAINT

The subject of the present invention is a
5 stable aqueous dispersion comprising one or a number of
hydroxylated fluorinated copolymers and optionally one
or a number of acrylic copolymers. These dispersions
have the advantage of being stable on storage, suitable
for forming films with excellent adhesion to various
10 substrates, of having good chemical properties and good
mechanical strength. In general they have the additional
advantage of possessing a high solids content, that is to
say greater than 30 % by weight.

These dispersions can be used as paints or
15 coatings which can be applied in particular according
to an electrodeposition process, as materials for
treating metals or fibres, for manufacturing paper and
cardboard, floor coverings, and the like.

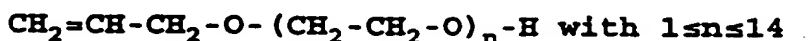
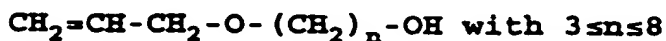
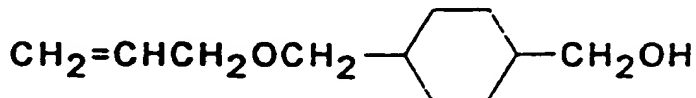
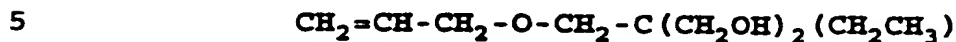
Such aqueous dispersions are described in
20 EP 212,508 and EP 224,870, on behalf of Daikin,
EP 341,716, on behalf of Asahi Glass, and EP 508,229,
on behalf of Central Glass; all these dispersions
contain an alcohol and a tertiary amine, such as
triethylamine. The presence of amine in a paint
25 composition has the disadvantage of leading to
yellowing of the paint during the film-forming heat
treatment or even the appearance of small holes at the
surface of the said paint.

EP 360,575, on behalf of JSR, describes solvent-free and amine-free aqueous dispersions in the vinylidene fluoride copolymer latex form prepared as an emulsion and seeded with an acrylic copolymer with a low glass transition temperature; the main defect of these dispersions is their lack of hardness, which is particularly injurious to paint applications.

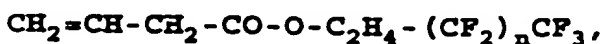
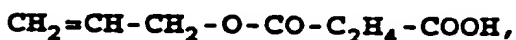
Fluorinated polymers are known for their chemical resistance, especially to solvents, their excellent thermal behaviour and resistance to bad weather and to radiation, for example UV radiation, their impermeability to gases and to liquids and their property as electrical insulators. They nevertheless have the disadvantage of being rather difficult to use, in particular for film-forming, with adhesion, transparency and impact resistance properties which are in general inferior to other thermoplastic polymers such as polyamides. The hydroxylated fluorinated copolymers which can be used for the aqueous dispersions according to the invention are in particular described in Patent Applications EP 396,445, EP 433,106 and EP 481,849 on behalf of the Applicant company: they derive from the following monomers:

1. from 45 to 95 % (molar) of vinylidene fluoride (VF2) and/or of trifluoroethylene (VF3),
2. from 5 to 55 % (molar) of tetrafluoroethylene (C_2F_4)
3. from 2 to 25 mol, per 100 mol of

monomers 1 + 2, of one or a number of hydroxylated allylic monomers chosen from allylic alcohol and hydroxylated allylic ethers such as



10 4. and from 0 to 10 mol, per 100 mol of monomers 1 + 2, of one or a number of monomers chosen from non-hydroxylated vinyl ethers, such as butyl vinyl ether, other fluorinated monomers (i.e. other than VF₂, VF₃ or C₂F₄), such as C₃F₆ or C₂F₃Cl, or non-salified allylic ethers and esters which are optionally carboxylated and/or substituted with $-(\text{CF}_2)_n-\text{CF}_3$ with $4 \leq n \leq 10$, such as:



The stable aqueous dispersions contain at least 30 % by weight of hydroxylated fluorinated copolymer(s).

The acrylic copolymer(s) according to the invention derive from the following monomers:

* from 40 to 70 % (by mass) of methyl methacrylate (MMA),

* from 30 to 60 % (by mass) of one or a number of alkyl (meth)acrylate(s), such as butyl acrylate (BuA) or the ethyl (meth)acrylates,

* and from 0 to 15 % (by mass) of one or a number of alkyl (meth)acrylate monomers which are functionalized or substituted, for example, with hydroxyl groups or $\text{CF}_3-(\text{CF}_2)_n-$ groups with $4 \leq n \leq 10$, such as hydroxyethyl (meth)acrylate (HEA), 2,2,2-trifluoroethyl methacrylate (TRIFEMA), $\text{CH}_2=\text{CR}-\text{COO}-\text{C}_2\text{H}_4-(\text{CF}_2)_n-\text{CF}_3$ with $\text{R}=\text{H}$ or CH_3 (CFnA), the (meth)acrylic acids (AA and MAA), the salts of 2-acrylamido-2-methylpropanesulphonic acid, in particular $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{SO}_3^- \text{N}^+(\text{C}_2\text{H}_5)_3$ (AMPS/TEA), dimethylacrylamide (DMA) or dimethylaminoethyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$ (MADAME).

Indeed, the Applicant company has noticed that the presence of some of the above monomers in the acrylic copolymer(s) improves certain mechanical, physical and/or chemical properties of the dispersion according to the invention. By way of example, hydroxy (meth)acrylates improve the crosslinking properties, TRIFEMA and the (CFnA)s have anti-graffiti properties, acrylic and methacrylic acids improve the adhesion properties, AMPS/TEA and DMA have properties of mechanical stabilization of the dispersion and MADAME makes it possible to coat substrates by cataphoresis.

The ratio by weight of the acrylic copolymer(s) to the hydroxylated fluorinated copolymer (s) and the acrylic copolymer (s) in the stable aqueous dispersion is between 0 and 50 % and preferably between 20 and 30 %.

5 The stability of the dispersion is provided for by one or a number of emulsifying agents present in the dispersion. Stable dispersion is understood to mean a dispersion which is stable with time, that is to say which can be used without detrimental change in its
10 properties after prolonged storage - of the order of a few months. The emulsifying agent(s) can be cationic, non-ionic and preferably anionic. The preferred anionic emulsifiers comprise $\text{CF}_3-(\text{CF}_2)_n-$ groups with $4 \leq n \leq 10$. Mention may be made, by way of example, of:

15 $\text{C}_n\text{F}_{(2n+1)}-\text{C}_2\text{H}_4-\text{SO}_3^-\text{K}^+$ $\text{C}_n\text{F}_{(2n+1)}-\text{COO}^-\text{K}^+$ $\text{C}_n\text{F}_{(2n+1)}-\text{COO}^-\text{NH}_4^+$

The stable aqueous dispersions generally contain from 0.5 to 3 % of emulsifying agent(s).

Another subject of the invention is processes for the preparation of stable aqueous dispersions of
20 hydroxylated fluorinated copolymers, on the one hand, and of hydroxylated fluorinated copolymers and of acrylic copolymers, on the other hand.

The literature teaches various methods for the preparation of stable aqueous dispersions. It is
25 possible to attach carboxyl functional groups to the hydroxylated fluorinated polymer chain, either by direct copolymerization or indirectly by chemical reaction of the hydroxyl functional groups. After

salification of the carboxylic acid functional groups, aqueous dispersions are obtained; see for example EP 212,508, EP 281,991, EP 320,156 and EP 508,229. It is also possible to copolymerize fluorinated olefins with macromers having units derived from ethylene or propylene oxide, as described in EP 341,716. The Applicant company has used the processes set out above with the fluorinated copolymers according to the invention and has observed that satisfactory aqueous dispersions, i.e. stable and with a high solids content and free of coagulates, are not obtained.

The process for the preparation of stable aqueous dispersions developed by the Applicant company consists in:

- preparing a solution of hydroxylated fluorinated copolymer(s), optionally in the presence of the acrylic copolymer(s), in an organic solvent,
- dispersing the solution thus obtained in an aqueous solution of emulsifying agent(s),
- removing the organic solvent, either simultaneously by distillation or after dispersion.

The organic solution of hydroxylated fluorinated copolymer(s) alone can in general be obtained by copolymerization of these copolymers directly in solution in the organic solvent; see, for example, EP 396,445, EP 433,106 and EP 481,849 on behalf of the Applicant company. The fluorinated copolymers can be polymerized in solution, in

particular in tert-butanol, methyl acetate or isopropyl acetate. After charging the organic solvent to the polymerization reactor, the hydroxylated allylic monomer(s) and then VF₂ and C₂F₄ are introduced. After having brought the temperature to between 50 and 70°C, the polymerization initiator, preferably chosen from isopropyl peroxydicarbonate or tert-butyl peroxy-pivalate, is added. During polymerization and in order to keep the proportions of the various monomers in constant ratios, VF₂, C₂F₄ and the hydroxylated allylic monomer(s) are added while taking care to keep the pressure constant. When all the monomers have been introduced, the temperature is lowered and the reactor is degassed, the unreacted fluorinated monomers being discharged. If the solvent used during the polymerization of the fluorinated copolymers is an acetate, the organic copolymer solution is suitable for being converted into an aqueous dispersion according to the invention. In contrast, if the solvent used is tert-butanol, it is necessary to carry out a solvent transfer in order to have available fluorinated copolymer in the desired solvent.

In the case of aqueous dispersions also comprising one or a number of acrylic copolymers, it is possible to mix the already synthesized acrylic copolymer(s) with the solution of hydroxylated fluorinated copolymer(s) or else to copolymerize the acrylic monomers (i.e. the monomers from which the

acrylic copolymer(s) derive(s)) directly in the organic solvent in the presence of hydroxylated fluorinated copolymer(s). The copolymerization of the acrylic copolymers in the solution of hydroxylated fluorinated copolymer(s) can be carried out by adding the entirety or a fraction of the acrylic monomers, which is introduced either continuously or by successive increments during polymerization. The polymerization temperature is in general between 40 and 90°C. It is possible to use transfer agents of mercaptan type in order to reduce the molecular masses and organosoluble radical initiators in general chosen from initiators of azo, peroxydicarbonate, peroxydipivalate and diacyl peroxide type. Mention may be made, as example, of azobisisobutyronitrile, cyclohexyl peroxydicarbonate or tert-butyl peroxydipivalate.

In the case of the aqueous dispersions also comprising one or a number of acrylic copolymers, a variant consists in using the seeded emulsion polymerization technique, such as described in EP 320,126 and EP 360,575, which consists in carrying out an emulsion polymerization of the mixture of acrylic monomers in the presence of hydroxylated fluorinated copolymer latex/latices or of an artificial dispersion of hydroxylated fluorinated copolymer(s).

The organic solvents according to the invention have a boiling point in general of between 30 and 90°C and a solubility in water of in general

between 0.5 and 500 g/l (measured at 20°C, NTP conditions). Mention may be made of alcohols or esters, the latter being particularly preferred by the Applicant company. As an example of preferred solvent, it is possible to use alkyl acetates (methyl acetate, ethyl acetate and isopropyl acetate, and the like).

The concentration by weight of the hydroxylated fluorinated copolymer(s) in the organic solvent is in general between 15 and 40 %.

Dispersion of the copolymers can be carried out using dispersers or homogenizers capable of dispelling a great deal of mechanical energy into the mixtures of immiscible liquids. These devices make it possible to produce emulsions of "oil-in-water" type by virtue of the addition of appropriate emulsifying agent(s), the "oil" phase being in this instance the organic solution of hydroxylated fluorinated copolymer(s). The aqueous solution/copolymer solution mixture is subjected to intense shearing by a mechanical stirring system or else by passing under pressure through nozzles. In general, the dispersion stage can be carried out within a temperature range of between 0 and 100°C and preferably between 15 and 50°C.

The water/copolymer solution ratio by weight is in general between 0.2 and 1.

After removal of the organic solvent, an aqueous dispersion is obtained which is stable on prolonged storage and which can be used several months

after its manufacture without lessening of its properties. The mechanical stability on storage of the aqueous dispersion can be assessed by carrying out, on the one hand, a sedimentation test and, on the other
5 ° hand, by measuring the size of the dispersed particles.

The sedimentation test consists in leaving the dispersion to stand for a month and in then evaluating the possible deposit formed after brief stirring followed by standing for 24 hours. The ratio
10 by weight of deposited and dried copolymers to the total amount of dried copolymers present is calculated.

The size of the particles is measured by analysis of the scattering of a monochromatic beam through a dilute sample of the dispersion.

15 Another subject of the invention is the use of the aqueous dispersions as binders for water paints. Water paints have undergone a recent blossoming due in particular to their ease of use (light equipment not requiring a system for removing the solvents, easy
20 cleaning of the equipment) and to a collective awareness of the problems of pollution of the environment. While the base constituents of paints, such as fluorinated polymers and acrylic polymers, are often soluble in organic solvents of ester or ketone
25 type, they are in general insoluble or virtually insoluble in water. There has therefore been a search to emulsify or disperse these essential constituents of paints so as to be able to use them in the aqueous phase.

In addition to the dispersions according to the invention, aqueous-phase paint binders comprise one or a number of hardeners which are in general resins carrying functional groups capable of chemically
5 reacting with the hydroxyl groups of the dispersed copolymers. Mention may be made, among hardeners which can be used in the context of the invention, of blocked or free polyisocyanate resins, it being necessary for the latter to be subjected to a pretreatment which
10 makes it possible for them to be emulsified in water, or melamine/formaldehyde or urea/formaldehyde resins.

The paints can also contain one or a number of pigments which can be of inorganic or organic type. It is preferable, in general, to use inorganic
15 pigments, among which mention may be made of titanium dioxide, iron or chromium oxides, mixed cobalt and aluminium oxides, carbon black, molybdate orange, corrosion-inhibitor pigments, such as zinc phosphate, or metallic pigments, such as aluminium.

20 The aqueous paints can also contain a small amount of solvent for the hydroxylated fluorinated copolymer(s), in order to improve the film formation thereof. Mention may be made, as example, of alcohols, ethers or ethers of glycol or of propylene glycol.

25 It is also possible to add, to the paint, any conventional adjuvant or additive for varnishes and paints, such as dispersing agents, thickeners of associative or non-associative type, agents intended to

promote spreading, rheology-modifying agents, heat-stabilizing and/or UV-stabilizing agents, antioxidants, anti-foaming agents, wetting agents for pigments and/or vehicles, fungicides, bactericides, antifreezes, catalysts of the hardening reaction of the paint, and the like.

The paint is prepared in a way known per se by mixing the various constituents. In general, the pigment(s) is/are dispersed in water, in the optional presence of dispersant(s), and then mixing is carried out at high speed until a dispersion having the required fineness is obtained. The preparation can be carried out in a disperser-type device where the liquids to be mixed are subjected to a high degree of shearing due to the intense stirring (Ultra-Turrax® device). It is also possible to obtain shearing by pumping the mixture of liquids to be dispersed through calibrated nozzles (Manton-Gaulin® device). It is also possible to disperse the liquids efficiently in an ultrasonic vessel of high frequency. Mention may also be made of electric dispersers where one of the phases to be dispersed is passed through a capillary placed in an electric field which disperses it in the form of fine droplets. The additive(s) listed above is/are then introduced with stirring, followed by the stable aqueous dispersion. Depending on the nature of the hardener, it is added either at the end of mixing or immediately before use of the paint. When the hardener,

for example a polyisocyanate, is introduced at the end of mixing, it is preferable to disperse it beforehand in water before introducing it into the mixture, in order to provide it with a better subsequent

5 distribution in the mixture. The predispersion of the hardener is further improved by diluting it beforehand in a solvent so as to decrease the viscosity and promote emulsification. Mention may be made, among the solvents which can be used, of esters, ether esters or
10 aromatic compounds. Solvents of low solubility are preferred because they are, in general, less liable to destabilize the emulsion of fluorinated copolymers. Solvent of low solubility in water is understood to mean solvents whose solubility in water is less than
15 30 % by weight.

The paints according to the invention can be applied to the substrates to be coated according to any known technique such as compressed-air spray gun, electrostatic, brush, roller, by curtain-coating, by
20 dipping or by electrodeposition.

The substrates to be coated can be metals (steel, galvanized steel, aluminium, and the like), plastics, such as PVC, polyesters or phenolic resins, glass, ceramics, wood or concrete, it being possible
25 for the said substrates optionally to be coated with primer and/or to be subjected to a surface treatment intended to promote adhesion of the paint, and the like.

In all the examples, the solids content (SC) is expressed in % by weight.

EXAMPLES 1 TO 11

Manufacture of aqueous dispersions containing hydroxylated fluorinated copolymers

Aqueous solution: 150 g of deionized water
containing 0.75 g of
emulsifier

Copolymer solution: 315 g of a solution of
the copolymer Ai or Cj
containing 23.8 % of
solids in the organic
solvent.

The characteristics of the copolymers Ai and Cj are indicated hereinbelow.

The aqueous emulsifier solution is introduced
into a 1 l beaker. This solution is stirred with an
Ultra-Turrax® disperser for a few seconds. The
copolymer solution is then introduced over 5 minutes at
a mean stirring speed of 6000 rev/min. Stirring is
continued for a further 1 minute at 10,000 rev/min and
then stirring is halted.

The dispersion is transferred into a 1 l
stirred reactor in which the solvent is removed by
distillation under vacuum at $T \leq 50^{\circ}\text{C}$.

No deposit or crust is formed during this
operation for the copolymers Ai.

The dispersion is drained off. The solids
content (SC) of the aqueous dispersion and the size of
the particles (mean diameter) are calculated and the

deposit formed after storing for 1 month is measured (gentle stirring is resumed and the dispersion is again left to settle).

Starting copolymers Ai and Cj Molar compositions[■]

5 According to the invention Ai

A1	VF2/C ₂ F ₄ /CH ₂ =CH-CH ₂ -O-CH ₂ -CHOH-CH ₂ OH	65/35/10
A2	VF2/C ₂ F ₄ /CH ₂ =CH-CH ₂ -O-(CH ₂) ₄ -OH	65/35/10
A3	VF3/C ₂ F ₄ /CH ₂ =CH-CH ₂ -O-CH ₂ -CHOH-CH ₂ OH	50/50/10
A4	VF2/C ₂ F ₄ /CH ₂ =CH-CH ₂ -O-CO-C ₆ H ₁₀ -COOH/	
10	CH ₂ =CH-CH ₂ -O-CH ₂ -CHOH-CH ₂ OH	50/50/2/10
A5	VF2/C ₂ F ₄ /C ₃ F ₆ /CH ₂ =CH-CH ₂ -O-CH ₂ -CHOH-CH ₂ OH	65/35/7/10

Comparatives Ci

C1	VF2/C ₂ F ₄ /C ₃ F ₆	78/22/7.5
C2	VF2/C ₂ F ₄ /CH ₂ =CH-O-C ₄ H ₉	65/35/10
15	C3 VF2/C ₂ F ₄ /CH ₂ =CH-CH ₂ -O-CO-C ₆ H ₁₀ -COOH	65/35/10

■ The molar proportions of the monomers, other than VF2 and C₂F₄, are indicated with respect to 100 mol of VF2 + C₂F₄.

TABLE 1

Example	Copolymer	Solvent	Emulsifier & with respect to the copolymer Al	% SC disper- sion	Particle size nm	Stability of the disper- sion. Degree of deposi- tion %
1	A1	Methyl acetate	$C_8F_{13}C_2H_4SO_3K$ 1 %	33	300	0
2	A4	Methyl acetate	$C_8F_{17}C_2H_4SO_3K$ 1 %	30	320	3
3	A3	Methyl acetate	"	33	300	3
4	A4	Methyl acetate	"	30	320	5
5	A5	Isopropyl acetate	"	30	350	10
6	A4	Methyl acetate	$C_8F_{13}COONH_4$ 1 %	30	250	15
7	A4	Methyl acetate	Na dodecyl- benzene- sulphonate 1 %	30	350	20
8	A1	Aceto- nitrile	$C_8F_{17}C_2H_4SO_3K$ 1 %	2 % O		90 % O
9	C1	Methyl acetate	$C_8F_{17}C_2H_4SO_3K$ 1 %	1 % O		95 % O
10	C2	Methyl acetate	$C_8F_{17}C_2H_4SO_3K$ 1 %	2 % O		90 % O
11	C3	Methyl acetate	$C_8F_{17}C_2H_4SO_3K$ 1 %	5 %	Not measurable	80 % O

o Separation by settling is very fast and the deposits cannot be redispersed; given that formation of the deposits is significant, the solids content of the

dispersion after 24 hours of sedimentation is low.

According to the teaching of EP 212,508,
EP 281,991, EP 320,156 and EP 508,229, the preparation
was also carried out of a 50 % by weight solution in
5 acetone of a copolymer A' containing

VF₂/C₂F₄/CH₂=CH-CH₂-O-CO-C₆H₁₀-COOH/CH₂=CH-CH₂-O-CH₂-
CHOH-CH₂OH units in the molar proportions 65/35/4/10,
where Mn=9000 and Mw=18,500, neutralized to 100 % with
triethylamine. Deionized water is added until the
10 solids content is 20 % and the acetone is then removed
under vacuum at 40°C. It is observed that the
dispersion loses its stability: a polymer mass is
formed which cannot be redispersed in water.

Aqueous dispersions containing hydroxylated
15 fluorinated copolymers and acrylic copolymers.

Starting fluorinated copolymers: Ai

Preparation of the acrylic copolymers ACRYL k

ACRYL 1 MMA/BuA/HEA copolymer

prepared in solution in methyl
20 acetate without the fluorinated
copolymer.

350 g of methyl acetate and 2.5 g of
cyclohexyl peroxydicarbonate are introduced into a 2 l
round-bottomed flask equipped with a double jacket, a
25 stirrer and a condenser.

After deaeration, the temperature is brought
to 50°C and the mixture of the following acrylic
monomers is introduced:

methyl methacrylate	75 g
butyl acrylate	75 g
hydroxyethyl acrylate	4.5 g

The mixture is run in over 1 hour and the
 5 polymerization is then continued for a further 3 hours.

A solution of acrylic copolymer in butyl acetate with a solids content of 27 % is recovered.

The composition by weight of the MMA/BuA/HEA copolymer is 48.5/48.5/3

10 ACRYL 2 MMA/BuA/AMPS copolymer

prepared in methyl acetate

300 g of methyl acetate, 65 g of methyl methacrylate, 65 g of butyl acrylate and a solution consisting of 20 g of AMPS, neutralized with 9.76 g of
 15 triethylamine, in 60 g of methyl acetate are introduced into a 2 l reactor equipped with a double jacket, a stirrer and a condenser. After deaeration, the temperature is brought to 50°C and 2.5 g of cyclohexyl peroxydicarbonate are added. Polymerization is
 20 maintained for 4 h at 50°C. 503 g of solution with a solids content of 30.9 % are recovered.

The composition by weight of the MMA/BuA/AMPS copolymer is 43.3/43.3/13.4.

25 ACRYL 3 MMA/BuA/HEA/MADAME copolymer,

67.5/67.5/5/10,

prepared in methyl acetate

365 g of isopropyl acetate and 2.5 g of azobisisobutyronitrile are introduced into a 2 l

reactor equipped with a double jacket, a stirrer and a condenser.

After deaeration, the temperature is brought to 70°C and the mixture of the following monomers is introduced:

methyl methacrylate	67.5 g
butyl acrylate	67.5 g
hydroxyethyl acrylate	5 g
MADAME	10 g

The mixture is run in over 1 h and the polymerization is continued for a further 3 h.

An acrylic copolymer solution with a solids content of 29.4 % is recovered.

The composition by weight of the MMA/BuA/HEA/MADAME acrylic copolymer is 45/45/3.3/6.7.

Solution of fluorinated copolymer and of acrylic copolymer

Preparation of acrylic copolymer in the presence of the fluorinated copolymer

600 g of a solution of copolymer A1, with a solids content of 25 %, in methyl acetate, and 1.8 g of cyclohexyl peroxydicarbonate, are introduced into a 2 l round-bottomed flask equipped with a stirrer, a double jacket and a condenser. After removing atmospheric oxygen, the temperature is brought to 50°C. The introduction of the mixture of following acrylic monomers is begun at this temperature:

methyl methacrylate	23.7 g
---------------------	--------

butyl acrylate	23.7 g
hydroxyethyl acrylate	1.5 g
dimethylacrylamide	1 g

This mixture is introduced steadily over

5 1 hour.

After polymerizing for 3 h at 50°C, the reactor is cooled. The F/A1 solution is drained off and is then ready to be dispersed.

The solids content is 30.7 %.

10 The fluorinated copolymer/acrylic copolymer ratio is 25 %.

The composition by weight of the MMA/BuA/HEA/DMA acrylic copolymer is 47.5/47.5/3/2.

15 Preparation of a solution containing the acrylic copolymer and the fluorinated copolymer by mixing (solutions F/A2 to F/A6)

The fluorinated copolymer, with a solids content of 25 %, and the acrylic copolymer ACRYL k (k = 1 to 3) are simply mixed so as to have acrylic
20 copolymer levels of the order of 30 % by weight. The details appear in Table 2.

Table 2

% Acrylic copolymer
(acrylic+fluorinated) copolymer:

No.	Fluorinated copolymer			Solvent	Acrylic copolymers				SC % of the dispersion
	Ref.	SC %	Weight (g)		Ref.	SC %	Weight (g)		
F/A2	A1	25	300	methyl acetate	ACRYL 1	27%	118.5	30	25.6
F/A3	A4	25	300	methyl acetate	ACRYL 1	27%	118.5	30	25.6
F/A4	A1	25	300	methyl acetate	ACRYL 2	30.9%	103.5	30	26.5
F/A5	A1	25	300	isopropyl acetate	ACRYL 3	29.4%	109	30	26.2
F/A6	A3	25	300	methyl acetate	ACRYL 1	27%	118.5	30	25.6

EXAMPLES 12 TO 17

Aqueous dispersions containing fluorinated copolymers and acrylic copolymers.

According to the procedure described in Examples 1 to 11, 315 g of a solution of fluorinated copolymer and of acrylic copolymer are dispersed with the disperser with deionized water containing 0.75 g of emulsifier of formula $C_nF_{2n+1}C_2H_4SO_3K$ ($n = 4$ to 10); the acetate solvent is then removed by distillation under vacuum.

Table 3

Example No.	Solvent	Water	Ref. solution	SC % aqueous dispersion	Size of the particles mm	Dispersion stability. Degree of deposition %/dry copolymer
12	Methyl acetate	150 g	F/A1 Sol	37 %	300	Stable 2 %
13	Methyl acetate	150 g	F/A2 Sol	41 %	290	Stable 1 %
14	Methyl acetate	150 g	F/A3 Sol	35 %	320	Stable 2 %
15	Methyl acetate	225 g	F/A4 Sol	31 %	250	Very stable 0 %
16	Isopropyl acetate	225 g	F/A5 Sol	30 %	310	Stable 5 %
17	Methyl acetate	225 g	F/A6 Sol	39 %	300	Stable 2 %

Examples 18 to 26 Aqueous-phase paints.

Example 18

A varnish is prepared in the following way:

The following are introduced into a 1 l

5 beaker:

* 2.4 g of a modified alkyl polyalkoxy ether
in paraffinic medium ① (viscosity 200 mPa·s)

* 0.7 g of a solution of
N,N'-dihydroxymethylurea, 1,6-dihydroxy-2,5-dioxohexane
10 and of an isothiazolinone derivative ②,

* 10 g of butyl diglycol acetate,

* 500 g of the fluorinated copolymer emulsion
of Example 1

and mixing is carried out at 500 rev/min for
15 1 minute.

An isocyanate predispersion is prepared
separately in a 500 ml beaker by successively -
introducing:

- 100 g of a hydrophilic aliphatic
20 polyisocyanate based on hexamethylene diisocyanate ③
(content of free NCO groups: 17.2 %, viscosity at 23°C:
3500 mPa·s)

- 122.2 g of water.

Vigorous mixing is carried out at 500 rev/min
25 for 1 minute.

178.9 g of this isocyanate predispersion are
then introduced into the above emulsion and stirring is
carried out at 500 rev/min for 1 minute in order to

obtain the varnish.

This varnish is applied with a 100 μ m spiral doctor blade to a plate of chromated aluminium, which has been degreased beforehand, and then stoved for
5 30 minutes at 80°C to give a film with a dry thickness of 16 μ m.

The Persoz hardness, measured according to NFT Standard 30-016, is 220 s.

The specular gloss at 60°C, measured
10 according to ASTM D 523-85, is 65 %.

The adhesion, evaluated according to NFT Standard 30-038, is Class 1.

The resistance to methyl ethyl ketone is greater than 100 to-and-fro movements.

15 In order to estimate the degree of crosslinking of the film, it is subjected to a series of rubbing movements with a cotton-wool swab impregnated with methyl ethyl ketone, until the substrate appears. A number of to-and-fro movements of
20 less than 50 indicates poor crosslinking and a number greater than 100 indicates excellent crosslinking.

Example 19

A white paint is prepared in the following way:

25 90 g of water and 1.8 g of a sodium polyacrylate ④ are introduced into a 1 l beaker, mixing is carried out and then 171.9 g of titanium dioxide are added.

Dispersion is carried out at 2000 rev/min for 15 minutes until a fineness of less than 10 μm is obtained.

The following are then introduced:

5 * 3 g of a modified alkyl polyalkoxy ether in paraffinic medium ① (viscosity 200 mPa·s)

 * 0.8 g of a solution of N,N'-dihydroxymethylurea, 1,6-dihydroxy-2,5-dioxohexane and of an isothiazolinone derivative ②,

10 * 10 g of butyl diglycol acetate,

 * 500 g of the fluorinated copolymer emulsion of Example 1

and mixing is carried out at 500 rev/min for 2 minutes in order to obtain a pigmented fluorinated emulsion.

15 The isocyanate predispersion is prepared separately in a 500 ml beaker by successively introducing:

 - 100 g of a hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate ③ (content of free NCO groups: 17.2 %, viscosity at 23°C: 3500 mPa·s)

20 - 30 g of methoxypropyl acetate

 - 92.2 g of water.

25 Vigorous mixing is carried out at 500 rev/min for 1 minute.

 178.9 g of this isocyanate predispersion are then introduced into the pigmented fluorinated emulsion

and stirring is carried out at 500 rev/min for 1 minute in order to obtain the paint. This paint is applied with a 120 μm spiral doctor blade to a plate of chromated aluminium, which has been degreased
5 beforehand, and then stoved for 30 minutes at 80°C to give a film with a dry thickness of 18 μm .

The Persoz hardness, measured according to NFT Standard 30-016, is 220 s.

10 The specular gloss at 60°, measured according to ASTM Standard D 523-85, is 30 %.

The resistance to methyl ethyl ketone is greater than 100 to-and-fro movements.

The adhesion, evaluated according to NFT Standard 30-038, is Class 0.

15 Example 20

A white paint is prepared in the following way:

80 g of water and 1.6 g of a sodium polyacrylate ④ are introduced into a 1 l beaker, mixing
20 is carried out and then 150 g of titanium dioxide are added.

Dispersion is carried out at 2000 rev/min for 15 minutes until a fineness of less than 10 μm is obtained.

25 The following are then introduced:

* 2.8 g of a modified alkyl polyalkoxy ether in paraffinic medium ① (viscosity 200 mPa·s)

* 0.7 g of a solution of

N,N'-dihydroxymethylurea, 1,6-dihydroxy-2,5-dioxohexane
and of an isothiazolinone derivative ②,

* 10 g of butyl diglycol acetate,

* 500 g of the fluorinated copolymer emulsion

5 of Example 2

and mixing is carried out at 500 rev/min for
2 minutes in order to obtain a pigmented fluorinated
emulsion.

The isocyanate predispersion is prepared
10 separately in a 500 ml beaker by successively
introducing:

- 100 g of a hydrophilic aliphatic
polyisocyanate based on hexamethylene diisocyanate ③
(content of free NCO groups: 17.2 %, viscosity at 23°C:
15 3500 mPa·s)

- 30 g of methoxypropyl acetate

- 92.2 g of water.

Vigorous mixing is carried out at 500 rev/min
for 1 minute.

20 143.1 g of this isocyanate predispersion are
then introduced into the pigmented fluorinated emulsion
and stirring is carried out at 500 rev/min for 1 minute
in order to obtain the paint.

This paint is applied with a 120 μ m spiral
25 doctor blade to a plate of galvanized steel with a
thickness of 0.8 mm, which has been degreased
beforehand and covered with a primer of epoxy type, and
then stoved for 15 minutes at 180°C to give a film with

a dry thickness of 17 μm .

The Persoz hardness, measured according to NFT Standard 30-016, is 245 s.

5 The specular gloss at 60°C, measured according to ASTM Standard D 523-85, is 38 %.

The resistance to methyl ethyl ketone is greater than 100 to-and-fro movements.

The adhesion, evaluated according to NFT Standard 30-038, is Class 0.

10 Example 21

A varnish is prepared in the following way:

The following are introduced into a 1 l beaker:

15 * 2.5 g of a modified alkyl polyalkoxy ether in paraffinic medium ① (viscosity 200 mPa·s)

* 0.7 g of a solution of N,N'-dihoxymethylurea, 1,6-dihydroxy-2,5-dioxohexane and of an isothiazolinone derivative ②,

* 10 g of butyl diglycol acetate,

20 * 500 g of the fluorinated copolymer emulsion of Example 12

and mixing is carried out at 500 rev/min for 1 minute.

25 The isocyanate predispersion is prepared separately in a 500 ml beaker by successively introducing:

- 100 g of the hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate ③

(content of free NCO groups: 17.2 %, viscosity 23°C:
3500 mPa·s)

- 122.2 g of water.

Vigorous mixing is carried out at 500 rev/min
5 for 1 minute.

149.6 g of this isocyanate predispersion are
then introduced into the above emulsion and stirring is
carried out at 500 rev/min for 1 minute in order to
obtain the varnish.

10 This varnish is applied with a 100 µm spiral
doctor blade to a plate of chromated aluminium, which
has been degreased beforehand, and then stoved for
30 minutes at 80°C to give a film with a dry thickness
of 18 µm.

15 The Persoz hardness, measured according to
NFT Standard 30-016, is 260 s.

The specular gloss at 60°, measured according
to ASTM Standard D 523-85, is 60 %.

The resistance to methyl ethyl ketone is
20 greater than 100 to-and-fro movements.

The adhesion, evaluated according to NFT
Standard 30-038, is Class 0.

Example 22

A white paint is prepared in the following
25 way:

100 g of water and 1.9 g of a sodium
polyacrylate ④ are introduced into a 1 l beaker, mixing
is carried out and then 194.6 g of titanium dioxide are

added.

Dispersion is carried out at 2000 rev/min for 15 minutes until a fineness of less than 10 μm is obtained.

5 The following are then introduced:

* 2.5 g of a modified alkyl polyalkoxy ether in paraffinic medium ① (viscosity 200 $\text{mPa}\cdot\text{s}$),

* 0.7 g of a solution of
N,N'-dihydroxymethylurea, 1,6-dihydroxy-2,5-dioxohexane
10 and of an isothiazolinone derivative ②,

* 10 g of butyl diglycol acetate,

* 500 g of the fluorinated copolymer emulsion
of Example 13

and mixing is carried out at 500 rev/min for
15 2 minutes in order to obtain a pigmented fluorinated
emulsion.

The isocyanate predispersion is prepared separately in a 500 ml beaker by successively introducing:

20 - 100 g of a hydrophilic aliphatic
polyisocyanate based on hexamethylene diisocyanate ③
(content of free NCO groups: 17.2 %, viscosity at 23°C:
3500 $\text{mPa}\cdot\text{s}$)

- 30 g of methoxypropyl acetate

25 - 92.2 g of water.

Vigorous mixing is carried out at 500 rev/min
for 1 minute.

162.3 g of this isocyanate predispersion are

then introduced into the pigmented fluorinated emulsion and stirring is carried out at 500 rev/min for 1 minute in order to obtain the paint. This paint is applied with a 100 μm spiral doctor blade to a plate of
5 chromated aluminium, which has been degreased beforehand, and then stoved for 40 minutes at 80°C to give a film with a dry thickness of 20 μm .

The Persoz hardness, measured according to NFT Standard 30-016, is 235 s.

10 The specular gloss at 60°, measured according to ASTM Standard D 523-85, is 39 %.

The resistance to methyl ethyl ketone is greater than 100 to-and-fro movements.

The adhesion, evaluated according to NFT
15 Standard 30-038, is Class 0.

Example 23

A white paint is prepared in the following way:

75 g of water and 1.6 g of a sodium
20 polyacrylate ④ are introduced into a 1 l beaker, mixing is carried out and then 141.5 g of titanium dioxide are added.

Dispersion is carried out at 2000 rev/min for 15 minutes until a fineness of less than 10 μm is
25 obtained.

The following are then introduced:

* 2.8 g of a modified alkyl polyalkoxy ether in paraffinic medium ① (viscosity 200 mPa·s),

* 0.7 g of a solution of
N,N'-dihydroxymethylurea, 1,6-dihydroxy-2,5-dioxohexane
and of an isothiazolinone derivative ②,

* 10 g of butyl diglycol acetate,

5 * 500 g of the fluorinated copolymer emulsion
of Example 15

and mixing is carried out at 500 rev/min for
2 minutes in order to obtain a pigmented fluorinated
emulsion.

10 The isocyanate predispersion is prepared
separately in a 500 ml beaker by successively
introducing:

- 100 g of a hydrophilic aliphatic
polyisocyanate based on hexamethylene diisocyanate ③

15 (content of free NCO groups: 17.2 %, viscosity at 23°C:
3500 mPa·s)

- 30 g of methoxypropyl acetate

- 92.2 g of water.

20 Vigorous mixing is carried out at 500 rev/min
for 1 minute.

25 104.7 g of this isocyanate predispersion are
then introduced into the pigmented fluorinated emulsion
and stirring is carried out at 500 rev/min for 1 minute
in order to obtain the paint. This paint is applied
with a 120 μ m spiral doctor blade to a plate of
chromated aluminium, which has been degreased
beforehand, and then stoved for 30 minutes at 80°C to
give a film with a dry thickness of 20 μ m.

The Persoz hardness, measured according to NFT Standard 30-016, is 200 s.

The specular gloss at 60°, measured according to ASTM Standard D 523-85, is 28%.

5 The resistance to methyl ethyl ketone is greater than 100 to-and-fro movements.

The adhesion, evaluated according to NFT Standard 30-038, is Class 0.

Example 24

10 A white paint is prepared in the following way:

75 g of water and 1.6 g of a sodium polyacrylate ④ are introduced into a 1 l beaker, mixing is carried out and then 142.7 g of titanium dioxide are added.

15 Dispersion is carried out at 2000 rev/min for 15 minutes until a fineness of less than 10 μm is obtained.

The following are then introduced:

*2.8 g of a modified alkyl polyalkoxy ether in paraffinic medium ① (viscosity 200 mPa·s),

20 *0.7 g of a solution of N,N'-dihydroxymethylurea, 1,6-dihydroxy-2,5-dioxohexane and of an isothiazolinone derivative ②,

*9 g of butyl diglycol acetate,

*500 g of the fluorinated copolymer emulsion of

25 Example 13

and mixing is carried out at 500 rev/min for 2 minutes in order to obtain a pigmented fluorinated emulsion.

The isocyanate predispersion is prepared separately in a 500 ml beaker by successively introducing:

- 100 g of a hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate ③ (content of free NCO groups: 17.2%, viscosity at 23°C: 3500 mPa·s)
- 20 g of propylene glycol diacetate
- 102.2 g of water.

Vigorous mixing is carried out at 500 rev/min for 1 minute.

119.6 g of this isocyanate predispersion are then introduced into the pigmented fluorinated emulsion and stirring is carried out at 500 rev/min for 1 minute in order to obtain the paint. This paint is applied with a 120 µm spiral doctor blade to a plate of chromated aluminium, which has been degreased beforehand, and then stoved for 30 minutes at 120°C to give a film with a dry thickness of 18 µm.

The Persoz hardness, measured according to NFT Standard 30-016, is 230 s.

The specular gloss at 60°, measured according to ASTM Standard D 523-85, is 33%.

The resistance to methyl ethyl ketone is greater than 100 to-and-fro movements.

The adhesion, evaluated according to NFT Standard 30-038, is Class 0.

Example 25

A varnish is prepared in the following way:

500 g of fluorinated copolymer of Example 1 are introduced into a 1 l beaker, followed by the addition of 210 g of a 10% solution of oxyethylenated alkylphenol ⑤ in water.

5 Mixing is carried out at 500 rev/min for 1 minute.

12 g of an associative thickener of polyurethane type are added to this dispersion, vigorous mixing is carried out at 500 rev/min for 1 minute, and then 47.5 g of a hydrophilic aliphatic polyisocyanate based on hexamethylene diisocyanate ③ (content of free NCO groups: 17.2%, viscosity at 23°C: 3500 mPa·s) are introduced dropwise into the dispersion with stirring at 1000 rev/min for 1 minute in order to obtain the varnish.

15 This varnish is applied with a 100 μ m spiral doctor blade to a plate of chromated aluminium, which has been degra. sed beforehand, and then stoved for 1 hour at 80°C to give a film with a dry thickness of 20 μ m.

20 The Persoz hardness, measured according to NFT Standard 30-016, is 215 s.

The specular gloss at 60°, measured according to ASTM Standard D 523-85, is 70%.

25 The adhesion, evaluated according to NFT Standard 30-038, is Class 1.

The resistance to methyl ethyl ketone is greater than 200 to-and-fro movements.

Example 26

A paint is prepared in the following way:

280 g of water and 0.69 g of a sodium polyacrylate
④ are introduced into a 1 l beaker, mixing is carried
5 out and then 138.25 g of titanium dioxide are added.

Dispersion is carried out at 2000 rev/min for
20 minutes until a fineness of less than 10 μm is
obtained.

The following are then introduced:

- 10 - 210 g of a 10% solution of oxyethylenated
alkylphenol ⑤ in water
- 3 g of a modified siloxane copolymer ①
- 0.8 g of a solution of N,N'-dihydroxymethylurea,
1,6-dihydroxy-2,5-dioxohexane and of an isothiazolinone
15 derivative ②
- 500 g of the copolymer dispersion of Example 1
- 12 g of an associative thickener of polyurethane
type.

Vigorous mixing is carried out at 500 rev/min for
20 2 minutes in order to obtain a pigmented fluorinated
emulsion.

47.5 g of a hydrophilic aliphatic polyisocyanate
based on hexamethylene diisocyanate ③ (content of free
NCO groups: 17.2%, viscosity at 23°C: 3500 mPa·s) are
25 then introduced dropwise into the dispersion with
stirring at 1000 rev/min for 1 minute in order to
obtain the paint.

This paint is applied with a 100 μm spiral doctor

blade to a plate of chromated aluminium, which has been degreased beforehand, and then stoved for 1 hour at 80°C to give a film with a dry thickness of 30 µm.

The Persoz hardness, measured according to NFT
5 Standard 30-016, is 200 s.

The specular gloss at 60°, measured according to ASTM D 523-85, is 40%.

The adhesion, evaluated according to NFT Standard 30-038, is Class 1.

10 The resistance to methyl ethyl ketone is 100 to-and-fro movements.

①: anti-foaming agent

②: bactericidal agent

③: hardener

15 ④: dispersing agent for the pigment

⑤: surface-active agent

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Stable aqueous dispersion comprising at least one emulsifying agent, characterized in that it comprises one or a number of hydroxylated fluorinated copolymers derived from the following monomers.

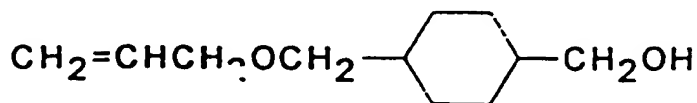
1. from 45 to 95 % (molar) of vinylidene fluoride (VF2) and/or of trifluoroethylene (VF3),

2. from 5 to 55 % (molar) of tetrafluoroethylene
10 (C₂F₄)

3. from 2 to 25 mol, per 100 mol of monomers
1 + 2, of one or a number of hydroxylated allylic
monomers chosen from allylic alcohol and hydroxylated
allylic ethers such as

15 $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{OH}$

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_n-\text{OH}$ with $3 \leq n \leq 8$

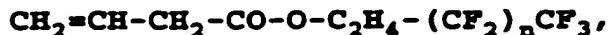
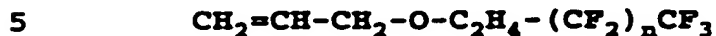
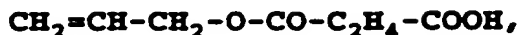


$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$ with $1 \leq n \leq 14$

$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O})_n-\text{H}$ with $1 \leq n \leq 14$

20 4. and from 0 to 10 mol, per 100 mol of monomers
1 + 2, of one or a number of monomers chosen from non-
hydroxylated vinyl ethers, such as butyl vinyl ether,
other fluorinated monomers (i.e. other than VF2, VF3 or
C₂F₄), such as C₃F₆ or C₂F₃Cl, or non-salified allylic
25 ethers and esters which are optionally carboxylated

and/or substituted with $-(CF_2)_n-CF_3$ with $4 \leq n \leq 10$, such as:



2. Stable aqueous dispersion according to Claim 1, characterized in that it comprises one or a number of acrylic copolymers derived from the following monomers:

*from 40 to 70 % (by mass) of methyl methacrylate (MMA),

15 *from 30 to 60 % (by mass) of one or a number of alkyl (meth)acrylate(s), such as butyl acrylate or the ethyl (meth)acrylates,

*and from 0 to 15 % (by mass) of one or a number of alkyl (meth)acrylate monomers which are functionalized or substituted, for example, with hydroxyl groups or $CF_3-(CF_2)_n-$ groups with $4 \leq n \leq 10$, the ratio by weight of the acrylic copolymer(s) to the hydroxylated fluorinated copolymer(s) in the stable aqueous dispersion being less than 50 % and preferably between 20 and 30 %.

25 3. Stable aqueous dispersion according to claim 1 or 2 characterized in that its solids content is at least 30 % by weight.

4. Process for the manufacture of the stable aqueous dispersions according to Claim 1 to 3 , characterized in that:

· a solution of hydroxylated fluorinated copolymer(s), optionally in the presence of the acrylic copolymer(s), in an organic solvent is prepared,

· the solution thus obtained is dispersed in an aqueous solution of emulsifying agent(s),

· the organic solvent is removed, either simultaneously by distillation or after dispersion.

5. Process for the manufacture of the stable aqueous dispersions according to Claim 2 or 3, characterized in that :

· the acrylic monomers are copolymerized in the presence of the hydroxylated fluorinated copolymer(s) in solution or in emulsion in an organic solvent,

· the solution thus obtained is dispersed in an aqueous solution of emulsifying agent(s),

· the organic solvent is removed, either simultaneously by distillation or after dispersion.

6. Use of the stable aqueous dispersions according to Claim 1 to 3 for the preparation of aqueous-phase paints and varnishes.

DATED this 30th day of May 1995.

ELF ATOCHEM S.A.

WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN. VIC. 3122.

A B S T R A C T

The invention relates to a stable aqueous dispersion comprising

*one or a number of hydroxylated fluorinated copolymers consisting of vinylidene fluoride and/or of trifluoroethylene, of tetrafluoroethylene, of one or a number of hydroxylated allylic monomers, and optionally of one or a number of monomers chosen from non-hydroxylated vinyl ethers,

*and optionally one or a number of acrylic copolymers consisting of methyl methacrylate and of one or a number of other alkyl (meth)acrylate(s), which are optionally functionalized or substituted.

It is prepared by dispersion in water of an organic solution of the above copolymers and then by removal of the organic solvent.

It can in particular be used as a binder for an aqueous-phase paint or varnish.